

Theoretical Study of Electronic and Structural Properties of Cu_nS_m Clusters

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Abstract

Small Copper Sulfide (Cu_nS_m) clusters were investigated, for this study we used density functional theory with *ab initio* pseudopotential and local density approximation. In this study basically we were calculated bond length, binding energy, HOMO-LUMO gap and density of state (DOS) for each of the most stable electronic structure of optimized geometries for different possible minimum-energy isomers of CuS cluster. From those of the candidate optimized geometries, a trigonal structure of CuS cluster were obtained as the most stable structure for many of the cluster sizes of the systems. Sulfur rich Cu_nS_m ($n=1,2,3$) has also been studied and visualized to understand the effects of Sulfur on CuS cluster by increasing the number of Sulfur atoms in the titled Clusters.

Keywords: HOMO-LUMO gap, Binding energy, DOS (density of state) and Bond length

Introduction

In the recent years, the development of efficient and reliable methods for studying matter at atomistic level has become an asset for important advancements in the context of material science. Both modern technological evolution and the need for new conception of materials and nanoscaled devices require a deep understanding of the properties of systems of many atoms from a fundamental viewpoint. To this aim, the support of computer simulation can be of great importance. Indeed, via computer simulation scientists try to model systems with many degrees of freedom by giving a set of “rules” of general validity (under some assumptions). Once these “rules” come from first-principles laws, these simulations have the ambition to model system properties from a fundamental viewpoint. With such a tool, the properties of existing materials can be studied in depth, and new materials and molecules can be conceived, with potentially enormous scientific and technological impact. [1, 2].

After the acceptance of atomic theory, the study of how matter behaves has divided into two streams. One has been reductionist, concentrating on the properties of individual atoms and molecules. In the 1930s this line led to nuclear physics and then to particle physics. The other stream has emphasized the properties of very many atoms or molecules together, so that the aggregates they make can be treated as infinite. The realm between these limits concerned only a few independent souls until about the late 1970s. Since then, interest has grown almost explosively in the study of what have come to be called clusters. This field constitutes one of the important areas where experiments and theoretical work go hand in hand and benefit considerably from each other's results [3].

The other very important thing is Nanotechnology which is a frequently used word both in the scientific literature and in the common language [4]. Indeed, nanotechnology is a word that stirs up enthusiasm or fear since it is expected for the good or for the bad, to have a strong influence on the future of mankind [5]. If one likes to have the shortest and most complete definition of nanotechnology one should refer to the statement by the US National Science and Technology Council [6] which states: The essence of nanotechnology is the ability to work at the molecular level, atom by atom, to create large structures with fundamentally new molecular organization. The aim is to exploit these properties by gaining control of structures and devices at atomic, molecular and supermolecular levels and to learn to efficiently manufacture and use these devices. In short, nanotechnology is the ability to build micro and macro materials and products with atomic precision [7].

The promise and essence of the nanoscaled science and technology is based on the demonstrated fact that materials at the nanoscale have properties (i.e. chemical, electrical, magnetic, mechanical and optical) quite different from the bulk materials [7]. Some materials exhibit unique physical, chemical, and biological properties at the nanoscale level (e.g. 1-100 nm) [8]. Those of the unique properties of nanomaterial originate from:

- Small dimensions, enabling for high speed and high functional density (nanoelectronics, lab-on-chip), small and lightweight devices and sensors (smart dust), high sensitivity (sensors, nanowires and special surface effects (such as lotus effect)).
- Very large surface area to volume ratio, providing reinforcement and catalytic effect.
- Quantum effects, such as highly efficient optical fluorescent quantum dots.
- New molecular structures, with new material properties: such as high strength nanotube nanofibers and nanocomposites [9].

Scientists from many disciplines are involved with studies related to atomic and molecular clusters [10].

This field constitutes one of the important areas where experiments and theoretical works go hand in hand and benefit considerably from each other's results [3]. In recent years, several binary and tertiary layered semiconductors have attracted a lot of interest due to their future optoelectronic applications in ultraviolet, visible and infrared regions of the spectra [11, 12]. Since these materials have large optical nonlinearity, they are also promising for optical switching devices. Besides, they can be used as photoelectric analyzers of polarized light, too [13]. Despite the significant number of experimental and theoretical studies on these materials, it is seen that neither the experimental data nor the overall theoretical understanding of them are sufficient to be qualified as a complete and coherent framework [14].

Among the family of group I of the transition metal and VI of non-metal, copper sulfide is an interesting material for its metal-like electrical conductivity, chemical-sensing capability and ideal characteristics for solar energy absorption [15, 16]. In this paper, as an interesting and essential contribution for the recent growth in science, we discuss the electronic and structural properties of isomers and different sized Cu_nS_m and sulfur rich CuS of minimum energy structures.

1. Theoretical Approach

1.1 The Many-Electron Problem and Quantum Mechanical Methods

The phrase many-electron problem describes the practical and theoretical difficulty of being able either to compute or write down an exact solution to the Schrodinger equation governing a system of interacting electrons. In a system of just two interacting particles, the Schrodinger equation is separable and can be solved exactly to obtain the motions of each particle. If a third particle or more is added to the system, however, the problem can no longer be solved analytically [17]. The goal of computational material science and also that of modeling nanoscale manmade structures is to calculate from first principles various physical and chemical properties. These properties can in principle be calculated by solving for the many-body wave function, which is a function of both the electronic and nuclear degrees of freedom [17].

Consider N nucleons of charge Z_n at positions R_n for $n = 1, \dots, N$ and M electrons at positions r_i for $i = 1, \dots, M$. An illustration is shown in Fig. 1.

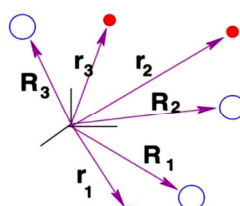


Figure 1: Atomic and electronic coordinates: filled circles represent electrons, open circles represent nuclei [18].

In order to describe the properties of crystals from first principle methods, we need to know the Hamiltonian of the system consisting of the number of electrons and nuclei:

$$H = -\hbar^2 \sum_i \frac{\nabla_i^2}{2m} - \hbar^2 \sum_I \frac{\nabla_I^2}{2M} + \frac{1}{2} \sum_{i,I} \frac{e^2}{|r_i - R_I|} + \sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|R_I - R_J|} \quad 1$$

Where r_i denotes the position of the i^{th} electron, R_I is the position of the I^{th} nucleus, Z_I is the atomic number of the nucleus. m is the mass of the i^{th} electron and M is the mass of the I^{th} nucleus respectively [18].

2. Computational Methods

2.1 Computer Simulations

Many aspects of computational modeling make it a worthy partner of experimental science. The chemist studying a particular reaction can reach into the computer simulation, alter bond lengths or angles, and then observe the effect of such changes on the process taking place. The geophysicist interested in phase transitions occurring deep inside the earth can model pressures and temperatures which could never be reached in a laboratory. All of this can be achieved with a single piece of apparatus - the computer itself.

Quantum-mechanical calculations stand out because they are by design *ab-initio* i.e. from first-principles, calculations. They do not depend upon any external parameters except the atomic numbers of the constituent atoms to be modeled and cannot therefore be biased by preconceptions about the final result. Such calculations are reliable and can be used with confidence to predict the behavior of nature.

Nevertheless, the same complexity which precludes exact analytical solution also results in the highly

unfavorable scaling of computational effort and resources required. The computational demands of exact calculations grow exponentially with the size of the system being studied, so that they are too costly to be of significant practical use. Despite the relentless progress of computer technology, this scaling makes this approach invisible for some time yet [19].

In this paper, VASP is used as the simulation tools for electronic structures of Copper Sulfid clusters. And we used a 20Å box size along the three coordinate system for this cluster simulation. The number of electrons considered in each species with their valance electron configuration is 3d¹⁰4s¹ for Cu and 3s²3p⁴ for S atom.

The code implements density functional theory (DFT). VASP is a package for carrying out *ab-initio* quantum mechanical simulations using pseudo-potentials (PP) with plane wave basis set. The input in VASP is the configuration of atoms enclosed in a cell which is periodically repeated. The simplest output is the electronic structure and energy of that configuration of atoms and the forces on the atoms. The electronic structure is a spatial array of electronic density and a population of electronic energy levels which can be integrated to give the electronic density of states. All plane waves with a kinetic energy smaller than E_{cut} are included in the basis set: i.e., $|k + G| \leq G_{cut}$ with $E_{cut} = \frac{G_{cut}^2}{2}$. The number of plane waves differs for each k-point and the number of k-points required for good convergence of the total energy and accurate k-space integration, depends on the size of the periodic system. For bigger unit cells, such as an artificial cell used for simulation of clusters, the reciprocal lattice is small and one k-point (which could be the Γ point) may be sufficient. In order to find the minimum energy, VASP performs a line minimization of the energy along the direction of the forces. A conjugate gradient algorithm is used to relax the atoms into their instantaneous ground state [20]. The convergence criterion is considered to be 10⁻⁴ eV for the total electronic energy. When the components of the forces on atoms are less than 0.01 $\frac{eV}{\text{\AA}}$ and the total energy convergence is tested for the plane-wave cutoff and the simulation cell size.

3. Result and Discussion

The structural differences in clusters from the bulk are also reflected in the electronic properties of the clusters. In a crystal, the electronic levels are quasi-continuous and form energy bands. In a small cluster, the levels are discrete; however, as the size of the cluster increases, the spacing between the discrete levels decreases and approaches a bulk-like electronic structure [21].

Copper Sulfide is formed by combining group B^I with A^{VI}. CuS is the most important semiconductor with a direct band gap of 2.5eV for bulk hexagonal wurtzite structure [22]. Here, at cluster size were studied by the density functional theory with *ab – initio* pseudo-potential and a local density approximation. Geometry optimizations starting from a number of initial candidate geometries were performed for each cluster size, so as a number of possible low energy isomers for each size. Among the lowest energy structures, we calculate the electronic and structural properties like bond length, binding energy, partial charge density and the HOMO-LUMO gap for the lowest energy. Variation of the electronic structure properties with different size has been investigated.

4.1 Electronic Structure Calculation for Cu_nS_m

In this section we present the structural and electronic properties of Cu_nS_m cluster. Copper Sulfid have different stoichiometry, ranging from Copper rich (Cu₂S) to sulfur rich (CuS₂), which have wide applications for example, we can use as p-type semiconductors, solar cells, and optical filters [23]. In this section we present the structural and electronic properties of CuS clusters using the methods presented below. The binding energy is the amount of energy related at its creation or the amount of energy we should need to add to the system in order to break it up. The binding energy of a certain cluster formed by two different atoms A and B is defined by:

$$BE(A_xB_y) = \frac{x E(A) + y E(B) - E(A_xB_y)}{x + y} \quad (2)$$

Where x and y will be the number of individual atoms, E(A) and E(B) are the minimum energy of the isolated atoms A and B respectively and $E(A_xB_y)$ is the minimum energy of the cluster.

The other method is to study the electronic structure of a certain cluster which is the partial charge density of the HOMO which is the occupied orbital of less energy and LUMO levels which is the next orbital with a higher energy and its gap (HOMO-LUMO gap). The definitions of such levels are described in Fig. 2 below.

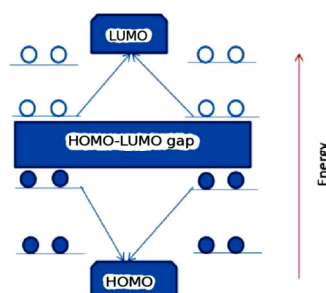


Figure 2: Definition of HOMO-LUMO level and the energy gap diagram

The number of electrons excited in to the conduction band is a function of the energy band gap E_g which is defined as the separation between the maximum energy in the valence band and the minimum energy in the conduction band. If E_g is small (0.3-4eV) a material is considered to be a Semiconductor and if E_g is large (4-12eV) a material is considered to be an insulator [24]. As the electrical and optical properties of a semiconductor are dependent on the energy gap, the data we get in this thesis is very important for semiconductor device design. The energy difference between the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) would be calculated by using:

$$[HOMO - LUMO]gap = bandgap = ELUMO - EHOMO \quad (3)$$

I. CuS (dimer)

Figure 3 demonstrates the optimized geometry and the partial charge density plot of CuS dimer with a bond length of 2.00Å. The binding energy and the HOMO-LUMO gap which is calculated using Eq.(2) and Eq.(3) respectively, is found to be 2.329 eV and 1.821 eV respectively. The partial charge density distribution of the HOMO and LUMO, as shown in Fig.3 indicates that the HOMO is localized mainly on S atom while the LUMO is distributed on both Cu and S atom. Table 1 shows the splitting of partial

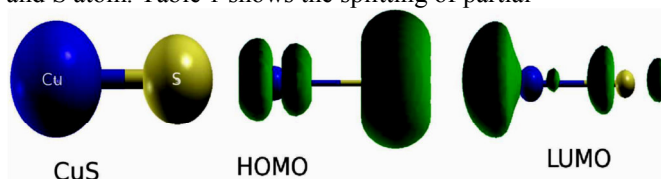


Figure 3: Partial charge density plots of the HOMO and LUMO orbitals of CuS (dimer).

Iso-surface plots are at 1/4th of the maximum value.

charge distribution in to s, p and d orbital for comparison with the DOS plot in Fig.4. This diagram tells us that there is high contribution of Cu atom of d orbital and p orbital contribution of S atom to the HOMO level of CuS dimer presented in Fig.3. As we can see in Table 1 of the calculated partial charge density for occupied and unoccupied.

Table 1: s, p and d partial charges within Cu and S spheres calculated for some occupied and unoccupied orbital in CuS dimer.

Orbital	Atom	s	p	d
LUMO+3	Cu	0.00	0.00	0.00
	S	0.00	0.00	0.00
LUMO+2	Cu	0.00	0.05	0.00
	S	0.00	0.02	0.00
LUMO+1	Cu	0.00	0.05	0.00
	S	0.00	0.02	0.00
LUMO	Cu	0.10	0.02	0.02
	S	0.00	0.10	0.00
HOMO	Cu	0.00	0.00	0.12
	S	0.00	0.31	0.00
HOMO-1	Cu	0.00	0.00	0.12
	S	0.00	0.31	0.00
HOMO-2	Cu	0.05	0.00	0.49
	S	0.00	0.07	0.00
HOMO-3	Cu	0.00	0.00	0.90
	S	0.00	0.00	0.00

orbital of CuS, there is high contribution of p orbital on the S atom on the HOMO and HOMO-1 but HOMO-2 and HOMO-3 are occupied by the d orbital of Cu atom. There is equal contribution of s orbital of Cu atom and p orbital of S atom to the LUMO level. HOMO and HOMO-1 levels are observed to fall to the same energy value. This can be compared with the DOS plot displayed in Fig.4

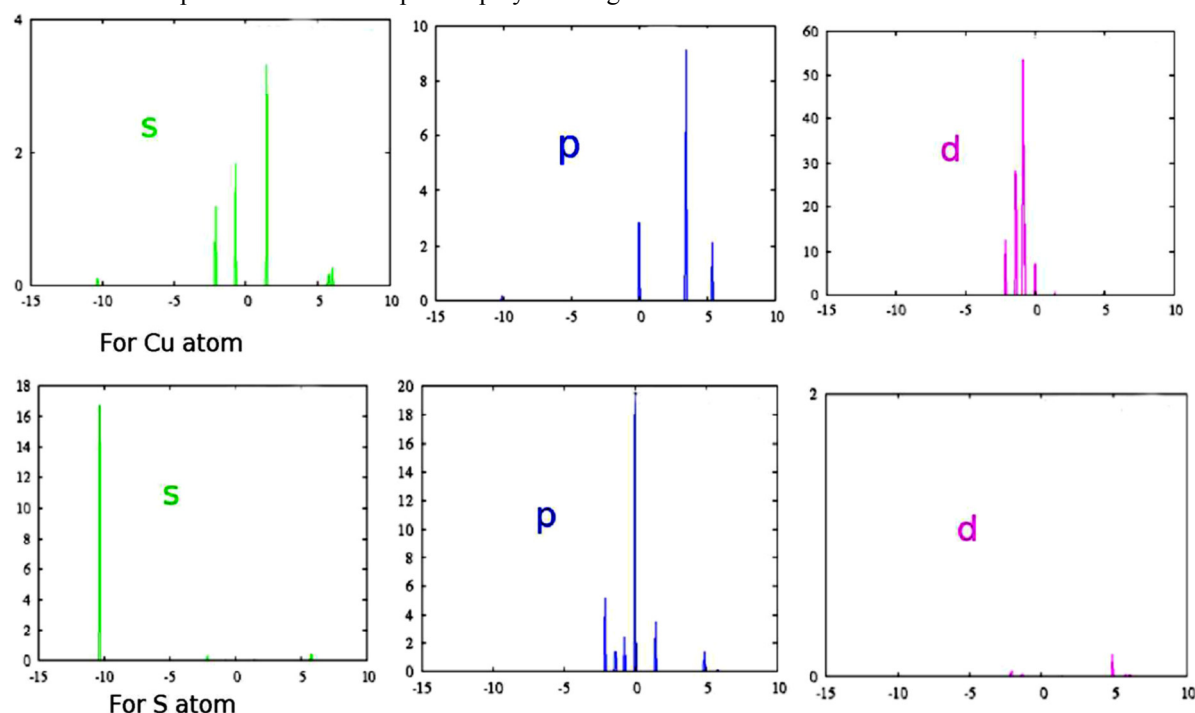


Figure 4: s, p and d orbital of Cu and S atoms contributed to the different levels. The discrete spectra are broadened by a Gaussian of width 0.01 eV. The upper pencil is for Cu atom and the lower one is for S atom.

II. Cu_2S_2 , Cu_3S_3 , Cu_4S_4

The optimized structures shown in Fig.5 have got different geometry with different number of atoms contributed for the formation of the titled clusters. From those structures we have found different values of binding energy, bond length, HOMO-LUMO gap energy, and partial charge density values for different geometry with different cluster size. Figure 5 shows the minimum energy geometry with their partial charge density plot.

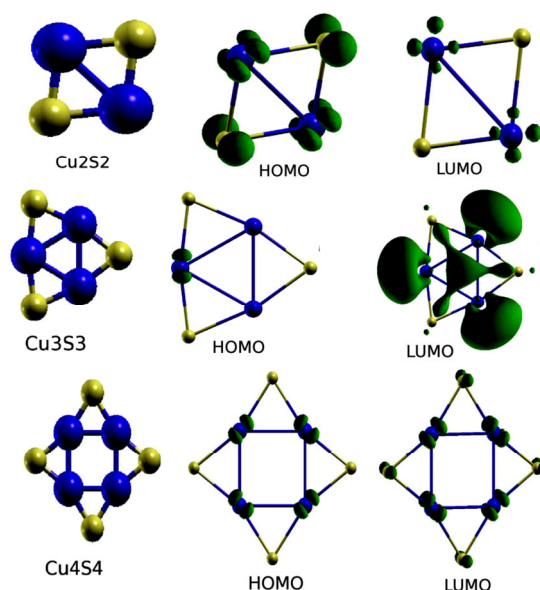


Figure 5 : Partial charge density plots of the HOMO and LUMO orbital of Cu_2S_2 , Cu_3S_3 and Cu_4S_4 . Iso-surface plots are at 1/4th of the maximum value.

As we can see in Fig. 5 Cu_2S_2 cluster has a rhombic structure and its Cu-Cu bond length is found to be 2.566 Å with the bond angle Cu-S-Cu and S-Cu-S is 76.139° and 103.760° respectively. In this structure the

HOMO are distributed on both Cu and S atoms but the LUMO are mainly localized on Cu atoms. The binding energy for Cu_2S_2 is found to be 3.525eV with band gap of 0.118eV. In Cu_3S_3 and Cu_4S_4 cluster, we observe that Cu_3S_3 has a trigonal structure with the central Cu-Cu-Cu form equilateral triangle of sides 2.49Å with a measured angle of Cu-S-Cu is 71.935° while Cu_4S_4 has nearly a rhombic structure with Cu-Cu bond length of 2.40Å. The average Cu-S bond length for Cu_3S_3 and Cu_4S_4 is found to be 2.097Å and 2.068Å respectively. The calculated binding energy for these two clusters is found to be 3.815eV and 4.050eV with a HOMO-LUMO gap of 4.377eV and 0.510eV. The partial charge distribution displayed in Fig.5 of Cu_3S_3 cluster shows occupation of the HOMO on a single Cu atom but the LUMO are largely distributed on all Cu atoms. In Cu_4S_4 there is all most equal distribution of the HOMO and the LUMO orbital on both Cu and S atoms.

III. Cu_5S_5 and Cu_6S_6

Figure 6 shows the optimized geometry and partial charge density plots of Cu_5S_5 and Cu_6S_6 . Both Cu_5S_5 and Cu_6S_6 are a 3D relaxed geometry, where Cu_5S_5 structure is a stack of two planar structures with average Cu-S bond length of 2.231Å and Cu_6S_6 is constructed by a stack of two six-membered rings in the chair conformation and is wurtzite structure with average Cu-S bond length of 2.189Å. The binding energy and HOMO-LUMO gap of Cu_5S_5 cluster is 4.299eV and 1.694eV respectively but for Cu_6S_6 corresponding values are found to be 4.351eV and 0.423eV. As shown in Fig.6, there is all most no distribution of HOMO on S atom of the two structures but there is small distribution of HOMO on Cu atoms in both cases. The LUMO are predominantly localized on the two pick Sulfur atom with a little distribution on the four central Cu atoms of Cu_5S_5 while in Cu_6S_6 the LUMO are localized on all of the Cu atoms, there is no occupation of LUMO on S atom.

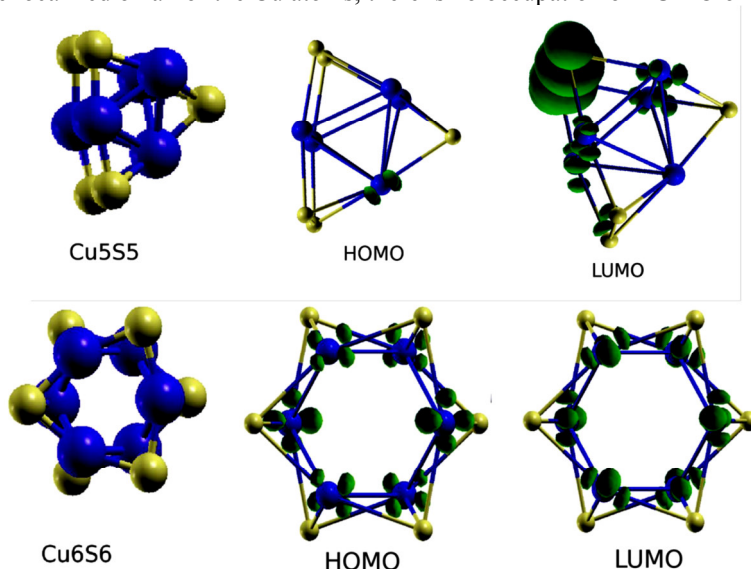


Figure 6: Partial charge density plots of the HOMO and LUMO orbitals of Cu_5S_5 and Cu_6S_6 . Isosurface plots are at 1/4th of the maximum value.

IV. Cu_8S_8 , Cu_9S_6 , $\text{Cu}_{10}\text{S}_{10}$ and $\text{Cu}_{16}\text{S}_{12}$ and $\text{Cu}_{20}\text{S}_{20}$

The minimum energy structure shown in Fig.7 has get some more interesting structure like Cu_8S_8 which is more or less perfect ring formed by two stacked rectangular structure. In this structure both Cu and S atom make inward and out ward bonding with each other to form such a shape with Cu-S bond length of 2.185Å. The HOMO-LUMO gap and binding energy is found to be 0.208eV and 4.382eV respectively. Cu_9S_6 get a crown like structure with a hexagonal base which is formed by only six Cu atoms.

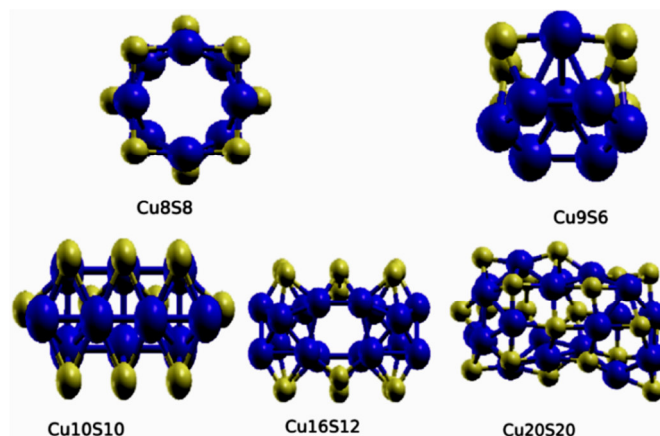


Figure 7: Optimized geometry for Cu_6S_8 , Cu_8S_8 , Cu_9S_6 , $Cu_{10}S_{10}$, $Cu_{16}S_{12}$ and $Cu_{20}S_{20}$

Table 2 shows the calculated binding energy, HOMO-LUMO gap energy, and average Cu-S bond length of Cu_nS_m clusters displayed in Fig.7. This table shows increase in binding energy with increasing number of CuS dimers in the cluster. The HOMO-LUMO gap energy is obtained by using the formula defined in Eq.(3) and the binding energy is calculated using Eq.(2).

Table 2: Binding Energy (eV), HOMO-LUMO gap (eV) and Average Bond length (Angstrom) of Cu_nS_m clusters.

Cluster	BE(eV)	HOMO-LUMO gaps(eV)	BL(Å) of Cu-S
CuS	2.329	1.821	1.999
Cu ₂ S ₂	3.525	0.118	2.078
Cu ₃ S ₃	3.815	4.377	2.097
Cu ₄ S ₄	4.050	0.5109	2.068
Cu ₅ S ₅	4.299	1.694	2.231
Cu ₆ S ₆	4.351	0.423	2.189
Cu ₈ S ₈	4.382	0.208	2.185
Cu ₉ S ₆	3.879	0.441	2.171
Cu ₁₀ S ₁₀	4.398	0.509	2.250
Cu ₁₆ S ₁₂	4.186	0.228	2.226
Cu ₂₀ S ₂₀	4.575	0.152	2.219

Figure 8 to 10 display, respectively, the plots of bond length, binding energy and HOMO-LUMO gap with respect to the number of atoms in CuS cluster. The average Cu-S bond length in CuS cluster should not exceeds 2.27Å[23]. This result is in agreement with our result in which average Cu-S bond length is less than 2.25Å. The binding energy has an increasing trend with increasing of the cluster size.

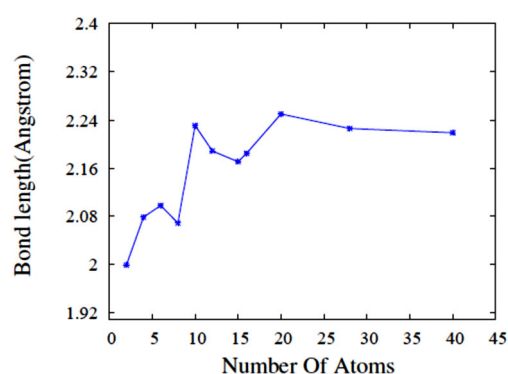


Figure 8: Average Cu-S bond length versus Number of atoms in Cu_nS_m clusters.

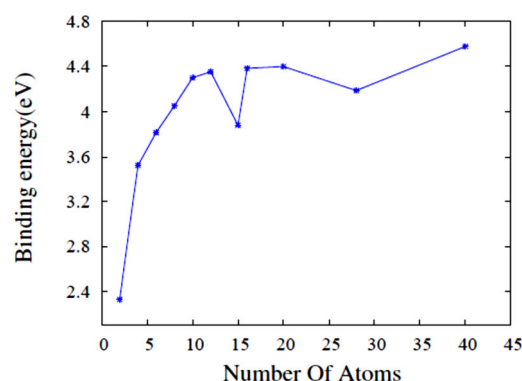


Figure 9: Binding energy versus number of atoms in Cu_nS_m clusters.

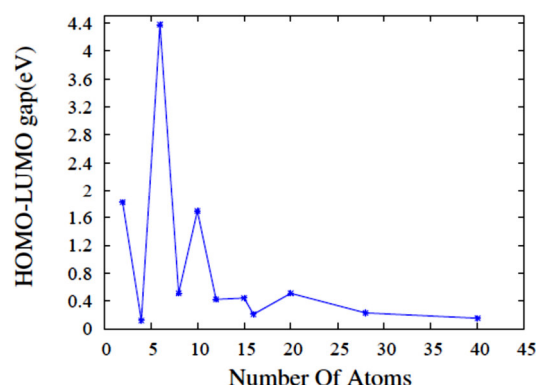


Figure 10: HOMO-LUMO gap versus number of atoms in Cu_nS_m clusters.

4.2 Electronic Structure Calculation for Sulfur Rich

Like what we have seen in section 4.4, we have investigated the effect of S atom on CuS cluster with respect to the structural and electronic properties, such as binding energy and HOMO-LUMO gap. In this sub-section the parameters are calculated by fixing the number of Cu atoms with increasing number of S atoms. From the minimum energy structure displayed in Fig.11, except CuS_3 and Cu_2S_6 other structures are found to be two dimensional.

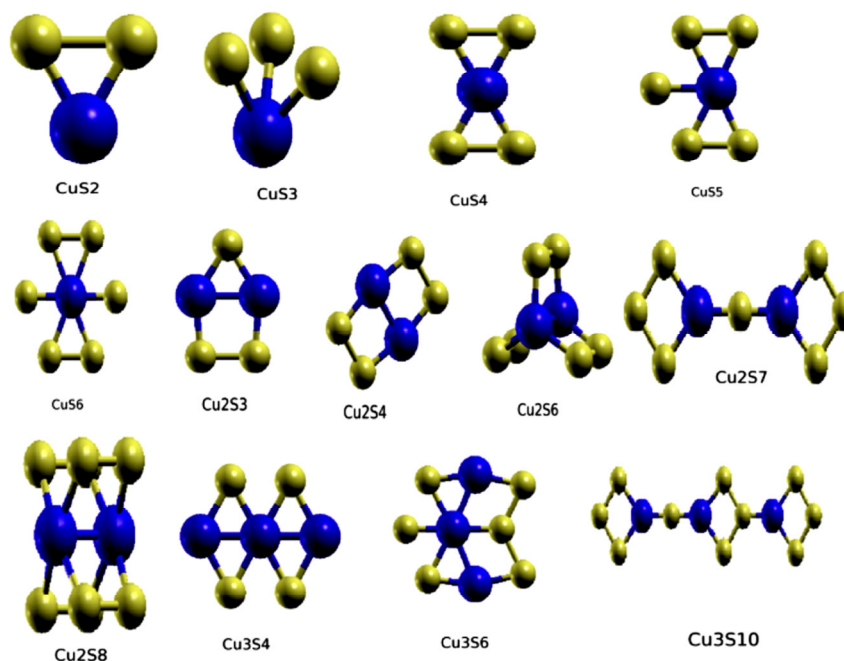


Figure 11: Optimized geometry for Sulfur rich Cu_nS_m clusters.

Here, the 3D minimum energy structure of CuS_3 cluster is found to be a trigonal structure with Cu-S bond length of 2.170\AA , in good agreement with Ohmasa *et al.* [25], 2.19\AA . As we displayed in Fig.11, most of the structures are constructed from trigonal and rhombic structures. To see the effects of S atom on CuS cluster, we have tabulated the calculated electronic properties for the minimum energy structures in Table 3, also their plots are shown in Fig.12.

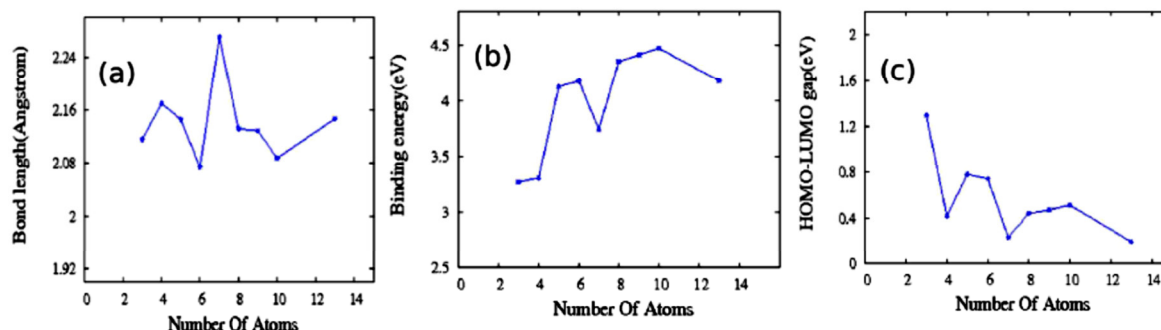


Figure 12: (a) Average Cu-S bond length, (b) binding energy and (c) HOMO-LUMO gap versus Number of atoms in Sulfur rich Cu_nS_m clusters (CuS_2 , CuS_3 , CuS_4 , Cu_2S_4 , CuS_6 , Cu_2S_6 , Cu_2S_7 , Cu_2S_8 and Cu_3S_{10}).

Table 3: Binding Energy (eV), HOMO-LUMO gap (eV) and Average Cu-S Bond length (Angstrom) of Sulfur rich Cu_nS_m clusters.

Cluster	BE(eV)	HOMO-LUMO gapss(eV)	BL(Å) of Cu-S
CuS_2	3.271	1.297	2.116
CuS_3	3.309	0.417	2.17
CuS_4	4.124	0.781	2.146
CuS_5	4.032	0.742	2.209
CuS_6	3.744	0.231	2.271
Cu_2S_3	3.801	3.326	2.125
Cu_2S_4	4.174	0.743	2.074
Cu_2S_6	4.351	0.442	2.132
Cu_2S_7	4.410	0.471	2.129
Cu_2S_8	4.470	0.514	2.088
Cu_3S_4	3.643	0.219	2.122
Cu_3S_6	4.107	0.708	2.174
Cu_3S_{10}	4.178	0.194	2.147

4. Summary and Conclusion

In order to obtain a better understanding of the electronic and structural properties of metal-non-metal combination cluster, we have performed a comprehensive study on CuS cluster by varying the size of the titled clusters. DFT-LDA pseudo-potential has been used for all calculations by the help of VASP software package.

In particular, we have investigated possible mechanisms for finding the minimum energy structures of Cu_nS_m in a single computer simulation. For those most stable structures we have found out the electronic and structural properties like bond length, binding energy, HOMO-LUMO gap and DOS of the systems.

A large HOMO-LUMO gap has been considered as an important prerequisite for the chemical stability of any cluster. With this concept among the minimum energy structure of Copper sulfide cluster, Cu_3S_3 possesses large HOMOLUMO gap. This indicates that this cluster gets high chemical stability while Cu_2S_2 possesses low HOMOLUMO gap among their cluster type. This small gap forced to have unstable chemical property.

As can be seen from the plot in Fig.8, the HOMO-LUMO gap shows a decreasing trend with cluster size. This is consistent with the fact that, as molecular orbital are formed from the overlap of more and more atomic orbital, the energy levels come closer. In other words the valence electrons are delocalized over more number of atoms as the cluster size increases [26]. In this study, we have observed that most of the optimized geometry of Cu_nS_m , HOMO-LUMO gap is in the range of 0.4eV to 4eV. This numerical value shows that Cu_nS_m has a valuable contribution for semiconductor designing.

In the study of the structural property of a certain cluster, measuring the bond length between two atoms tells us that one of the structural properties of that cluster but whatever we measure the average bond length of a cluster, it will never be above the bulk bond length. Fig. 8 shows the increasing trend of bond length with increasing of cluster size but the maximum average bond length is found to be 2.25\AA at $\text{Cu}_{10}\text{S}_{10}$ for Cu_nS_m and the minimum bond length calculated is at dimer structure which is found to be 1.999\AA . Since increasing number

of atoms in a cluster increases the neighboring atom interaction in a certain cluster. Due to this increment of the neighboring interaction energy, the energy we need to break the bond between one another will increase that is the binding energy of the cluster. As we shown in Fig.9, it has an increasing trend with increasing of cluster size.

From the results obtained, it could be concluded that Copper Sulfide clusters in nano size have novel electronic and structural properties that differ from the bulk. Therefore, the electronic structures of CuS cluster can be affected by the surface reconstruction, the size and the geometry of the cluster. Therefore, the band gap (HOMOLUMO gap) of the cluster can be controlled by manipulating their size and shapes.

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